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13. ABSTRACT (Maximum 200 words) Ignition in nonpremixed counterflowing jets of fuel against heated air has been investigated experimentally, computationally, and analytically. Using H ₂ /air ignition as the primary test system, the dominant chemical kinetics of ignition has been identified as well as the role of temperature, pressure, aerodynamic straining, and fuel concentration on the ignition process. In addition, the coupling of mass transport and aerodynamic straining to the chemical kinetics in nonpremixed ignition has been clarified. The methodologies developed for investigating hydrogen/air ignition have been extended to ignition of more complex and realistic fuels such as methane, n-butane, and iso-butane. DTIC QUALITY INSPECTED 2			
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**Ignition Studies in Non-Premixed
Hydrocarbon/Air Combustion**

Final Technical Report

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1/24/94

U. S. Army Research Office
(Proposal: 27565-EG; Grant: DAAL03-90-G-0222)

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Table of Contents

Statement of the Problem Studied.....	1
Summary of the Most Important Results.....	2
1. Experimental Investigations.....	2
2. Computational Simulations.....	4
3. Analytical Studies.....	8
Additional Research Accomplishments.....	8
1. Structure of Heptane-Air Flames.....	8
2. Methanol and Ethanol Reaction Mechanisms.....	9
3. Combustion of Methanol and Ethanol Droplets.....	9
Publications.....	10
1. Journal Publications.....	10
2. Meeting Papers and Technical Reports.....	10
Scientific Personnel.....	12
Report of Inventions.....	12
Bibliography.....	13
Figures.....	14

Statement of the Problem Studied

Recognizing the importance of ignition in diesel combustion, we have actively pursued an ARO-sponsored research program during the past three years that investigates ignition in convective-diffusive systems. Our research seeks to provide fundamental understanding of the process of forced ignition in nonuniform, diffusive and pressurized media, particularly in the coupling between chemistry and mass transport. The challenge is to integrate results and insights obtained from the purely chemical systems of auto-ignition into the diffusive systems of forced ignition, and interpret both phenomena from a unified viewpoint and apply this understanding to modelling and optimizing the ignition event in diesel engines.

Summary of the Most Important Results

During the course of the research, we have developed many useful methodologies and tools for experimentally, computationally, and analytically studying the chemical kinetics and dynamics of nonpremixed ignition in aerodynamically-strained flow fields. Using H_2 /air ignition as our primary test system, we have identified the dominant chemical kinetics just prior to ignition, the influence of temperature, pressure, and fuel concentration on ignition, and the role of mass transport and aerodynamic straining, as well as their coupling to chemical kinetics in the ignition process. These methodologies have been extended to investigations of forced ignition in more complex fuels such as methane, n-butane, and iso-butane.

In order to study ignition in a nonuniform, diffusive medium, we have adopted the counterflow configuration created by impinging two jets against each other. Both nonpremixed and premixed ignition can be studied. The counterflow configuration, which has been extensively adopted recently in flame studies, has the following advantages. First, the flow field is steady and basically quasi-planar, which not only simplifies experimentation and computation, but also facilitates data reduction and interpretation. Second, the counterflow has a well-defined, constant strain rate given by its velocity gradient, a , which can be used to quantify the effects of flow nonuniformity. Third, since the counterflow velocity field varies linearly with distance, it frequently represents the leading-order non-constant term in a Taylor-expansion of an arbitrary nonuniform flow field. Thus, data obtained from a counterflow study can be frequently used, to leading order, in situations involving other flow fields.

1. Experimental Investigations

The ignition state in nonpremixed counterflowing jets of fuel against hot air has been mapped out as function of global parameters such as air temperature, imposed strain rate, and

system pressure. Ignition measurements have been made for a variety of fuels such as hydrogen, methane, n-butane, and isobutane.

Figure 1 shows a schematic of the variable-pressure (0.1-15 atm), opposed-jet, counterflow ignition apparatus specifically designed and constructed for this research. The lower burner consists of concentric quartz tubes and Inconel screens which direct the cold jet (fuel for nonpremixed ignition and fuel/oxidizer for premixed ignition) upward, surrounded by an N_2 guard flow. The upper jet (oxidizer for nonpremixed ignition and inert for premixed ignition) is similarly configured, and is further equipped with both internal and external electric heating elements which are capable of raising the temperature of the downward flowing jet to ~ 1600 K. Long term stability is approximately ± 1 K. The burners are rigidly held by a stage that allows for fine adjustments along multiple axes (x, y, z, angular) in order to achieve optimal flow symmetry. Two-dimensional flow field imaging using $0.3 \mu m$ alumina particles and a focused sheet of laser light are used to guide flow adjustments. Single-point laser Doppler velocimetry is used to measure the axial flow velocity while the axial temperature profiles are currently measured using thermocouples. The turbulence intensity of the flow is less than 1%.

In achieving ignition, the concentrations and mass flow rates of the two jets are held fixed while the temperature of the hot jet is gradually increased. Figure 2 plots the measured ignition temperature of a jet of 20% hydrogen in nitrogen against heated air as a function of a representative strain rate at three different system pressures. At all pressures, the ignition temperatures are found to increase monotonically with increasing strain rate. It may also be seen that the sensitivity of the ignition temperature to strain rate is larger at high and low pressures than it is at one atmosphere. The relative insensitivity of the ignition temperature to variations in the strain rate at one atmosphere, discussed below, is due to extremely fast chemical reactions which dominate the ignition

process. In the more normal case, represented here at both higher and lower pressures and also seen typically in other fuels, chemical times are comparable to residence times and thus strain-dependent transport processes play an important role in the ignition process. Ignition temperatures, plotted as a function of pressure for a fixed strain rate are seen in Fig. 3 to exhibit a 'Z'-shape characteristic of the explosion limits for homogeneous hydrogen-air mixtures. As discussed below, this is found to be a consequence of the fact that the dominant chemistry is identical for both homogeneous explosions and inhomogeneous ignition.

Experimental measurements of the ignition temperature as a function of both strain rate and fuel concentration have also been performed for nonpremixed methane, n-butane, and iso-butane ignition at atmospheric pressure. The ignition of methane is particularly difficult, as is well known, and it should be considered a special accomplishment that we have been able to ignite methane by using electrically heated air. As mentioned above, the ignition temperatures for these hydrocarbon fuels show significantly greater sensitivity to strain rate variations than was seen for one atmosphere hydrogen. N-butane was also found to ignite more easily than iso-butane, as would be expected from their relative knocking tendencies.

2. Computational Simulations

Computational simulation of nonpremixed hydrogen ignition with detailed chemistry and transport has been conducted by using a modified version of the diffusion flame code of Smooke and co-workers [1,2] which employs adaptive gridding and a combined Newton method/time integration solution scheme. The hydrogen oxidation mechanism of Yetter et al. [3] is employed, involving 9 species and 19 reversible reactions. The ignition temperature is determined in the manner of the experiments, through gradual increase in the hot jet temperature until the concentration of such crucial radicals as H starts to increase rapidly with minute changes in the temperature.

Figure 4 is a representative ignition boundary as function of the system pressure and ignition temperature. As seen experimentally (see Fig. 3) the ignition response in this forced-ignition, diffusive system exhibits a characteristic 'Z'-shape that is similar to that exhibited by the explosion limits for homogeneous hydrogen/air mixtures. Specifically, for a given temperature of the hot jet, increasing pressure from a low value can render a non-ignitable mixture to become ignitable, then non-ignitable, and finally ignitable again. This correspondence shows that, despite the globally nonpremixed configuration studied, ignition shares many characteristics of premixed, homogeneous explosions. It is therefore of particular interest and significance to interpret and relate results from this nonpremixed system to the homogeneous system. We shall do so for the three ignition limits observed.

We first discuss the second ignition limit. Figure 5 shows typical concentration profiles of some important species. These profiles can be grouped into two categories, namely "steady-state" and "sink" profiles. The species in the first category: O, H, and OH, exhibit narrow peaks because they are found to be in "steady-state", i.e. their chemical creation and destruction rates are significantly larger than the characteristic rates for mass transport. These overlapping profiles of critical radical species are identified as the spatially localized 'ignition kernel'. "Sink" profiles, exhibited by H_2O and HO_2 , are substantially broader than the steady-state profiles and typically extend beyond the stagnation point. Such species are relatively stable and act as sinks for the radicals formed within the ignition kernel. The dominant chemistry in this second ignition limit is thus the same as that for the second explosion limit for the homogeneous mixture, being governed by the competition between the $H+O_2$ chain branching versus $H+O_2+M$ chain termination reactions. Indeed, it is seen in Fig. 4 that the calculated second ignition limit lies close to the well-known second explosion limit (shown as a dotted line). Thus the second ignition limit is chemistry controlled, with transport having only a very small effect.

Figure 6 shows the profiles of the important species for the first ignition limit, which is relevant at low pressures. Here we see that the crucial radical H assumes a broad profile, diffusing beyond the stagnation plane. Since the H radicals are not totally consumed in the ignition kernel, they are considered to be lost to the ignition process. Thus, in analogy to the first explosion limit in which the radicals are destroyed at the walls of the explosion vessel at low pressures, at the first ignition limit the radicals are diffusively-lost from the ignition kernel. Thus the first ignition limit depends on both chemistry and transport.

Figure 7 shows the species profiles for the third ignition limit, which is relevant in the high pressure regime. Again, in analogy with the third explosion limit, the fate of the H_2O_2 radical becomes important. In this regime, ignition is controlled by the competition between relatively slow collisional decomposition of H_2O_2 into 2OH versus convective transport out of the ignition kernel. In this way the third ignition limit is again controlled by both chemistry and transport.

Figure 8 shows the 'Z'-shaped ignition curves for a range of strain rates. It is seen that while the first and third limits are significantly affected by the strain rate, the second ignition limit follows closely the second explosion limit, hence further substantiating the above discussion on the controlling mechanisms for the three ignition limits. Figure 9 shows the ignition temperature as a function of the strain rate for three different pressures. It is seen that the ignition temperature is insensitive to the strain rate at 1 atmosphere, except for very high strain rates. Such insensitivity is due to the fact that the system is close to the second ignition limit at one atmosphere, and hence is controlled by chemistry but not by transport.

In a further study, full system response S-curves for a hydrogen-air diffusion flame were calculated at pressures of 0.1, 1, and 10 atmospheres to investigate the role of chemical heat release in providing 'thermal feedback' at the ignition turning point. Contrary to classical notions based upon one-step overall chemistry, thermal feedback was found to play essentially no role

in the steady-state solution at the ignition turning point - either in its character or parametric dependence. This can be seen in Fig. 10 where the peak hydrogen mole fraction, the maximum temperature of the system, and the local increase in temperature due to heat release are all graphed as a function of the air temperature for 60% hydrogen at one atmosphere. It can be readily seen that the response of the S-curve around the ignition turning point is identical whether or not chemical heat release is included in the calculation. In the majority of cases studied, turning point and S-curve behavior were found to exist in the complete absence of heat release, driven solely by 'kinetic' feedback provided by nonlinearities in the coupled chemical kinetics. As a result, the location of the ignition turning points is essentially governed by the kinetics of gain versus loss of key radicals in the ignition kernel which depend parametrically upon global variables such as air temperature, strain rate, pressure, and fuel concentration. One cause of this phenomena is the extremely small size of the radical pool at the ignition turning point, which necessarily limits the degree of localized heat release and temperature perturbation. The small radical pool is also found to decouple the problem such that, on the lower branch and around the ignition turning point, the temperature and possibly major species profiles may be solved independently of the complex chemistry involving the minor species. Furthermore, since heat release is not significant at the ignition turning point, the *transient* ignition process (in which the system evolves to a diffusion flame from the turning point) must begin with an induction period wherein the radical pool increases via essentially isothermal chemical kinetics before thermal feedback can ensue.

Manuscripts summarizing this work has been prepared and submitted for journal publication (Publication Nos. 1 and 2). We have in addition also performed preliminary calculations for nonpremixed methane ignition. These results are now being interpreted on the basis of chemistry and transport coupling.

3. Analytical Studies

Asymptotic analysis has also been performed for nonpremixed hydrogen ignition, using reduced mechanisms. The starting mechanism is that of Trevino [4], which consists of eight reaction steps and eight species (H , H_2 , O , O_2 , OH , H_2O , HO_2 , H_2O_2). In the first limit, steady-state approximation is made for OH , O and H_2O_2 but not for H and HO_2 . Thus the starting mechanism is reduced to a three-step mechanism. For the third ignition limit, the steady-state approximation is made for H , OH , O and HO_2 , but not for H_2O_2 , leading to a two-step reduced mechanism. Solution of the analysis basically reproduces the qualitative aspects of the computed results, as shown in Fig. 11.

A manuscript summarizing the work has been for journal publication (Publication No. 3).

Additional Research Accomplishments

In addition to research on ignition, several other research projects have been accomplished under ARO sponsorship. Specifically, a numerical study on the structure of heptane/air flames has been completed. The understanding gained will prove useful for latter studies on the ignition of liquid fuels. Three projects have also been completed on alcohol fuel combustion, which is of interest to the Army. These works are briefly summarized in the following.

1. Structure of Heptane-Air Flames

Numerical calculations were performed using a simplified chemical kinetic mechanism to determine the structure of counterflow, heptane-air diffusion flames. The predicted structure using a starting mechanism consisting of forty elementary steps was found to agree reasonably well with previous measurements. Reduced mechanisms, consisting of six and four steps, were deduced from the elementary mechanism. Calculated

flame structure using these reduced mechanisms were also found to agree well with those obtained with the starting mechanism. This work is reported in Publication No. 4.

2. Methanol and Ethanol Reaction Mechanisms

Comprehensive experimental and computational studies have been performed for the oxidation kinetics of methanol and ethanol. The studies involve experimental determination of the laminar flame speeds of these alcohols, and the compilation of detailed mechanisms describing their oxidation kinetics, using the most recent kinetic information. These schemes were tested against the experimental data for the propagation speed and structure of flames as well as the species concentration evolution in flow reactors, static reactors, and shock tubes. Satisfactory agreements were obtained, supporting the usefulness of the compiled schemes.

These works are reported in Publication Nos. 5 and 6.

3. Combustion of Methanol and Ethanol Droplets

The vaporization and combustion of freely-falling methanol and ethanol droplets in dry and humid environments were studied experimentally. From time-resolved measurements of droplet size and composition, it is demonstrated that water vapor, either from the ambience or generated at the flame, can freely condense at the droplet surface and subsequently dissolve into the droplet interior. The associated condensation heat release and dilution of the droplet alcohol content can significantly modify the droplet gasification behavior from that of the d^2 -law.

This work is reported in Publication No. 7.

Publications

Journal Publications

1. "Ignition in nonpremixed counterflowing hydrogen versus heated air: Computational study with detailed chemistry," by T. G. Kreutz and C. K. Law, submitted.
2. "The role of kinetic versus thermal feedback in nonpremixed ignition of hydrogen versus heated air," by T. G. Kreutz, M. Nishioka, and C. K. Law, submitted.
3. "Asymptotic analysis of ignition in nonpremixed counterflowing hydrogen versus heated air," by S. R. Lee and C. K. Law, Combustion Science and Technology, in press.
4. "Numerical description of the structure of counterflow heptane-air flames using detailed and reduced chemistry with comparison to experiment," by H. K. Chelliah, M. Bui-Pham, K. Seshadri and C. K. Law, Twenty-Fourth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 851-857 (1992).
5. "A comprehensive study of methanol kinetics in freely-propagating and burner-stabilized flames, flow and static reactors, and shock tubes," by F.N. Egolfopoulos, D. X. Du and C. K. Law, Combustion science and Technology, Vol. 83, pp. 33-75 (1992).
6. "A study on ethanol oxidation kinetics in laminar premixed flames, flow reactors, and shock tubes," by F. N. Egolfopoulos and C. K. Law, Twenty-Fourth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 833-841 (1992).
7. "An experimental investigation on the vaporization and combustion of methanol and ethanol droplets," by A. Lee and C. K. Law, Combustion Science and Technology, Vol.86, pp. 253-265 (1992).

Meeting Papers and Technical Reports

1. "Intrinsic Transport and Chemistry Coupling in Combustion Processes," C. K. Law, F.N. Egolfopoulos, and T. G. Kreutz,

Proceedings of the 6th Toyota Conference on Turbulence and Molecular Processes in Combustion, Shizuoka-ken, Japan, 11-14 October 1992.

2. "Ignition in Nonpremixed Counterflowing Hydrogen versus Heated Air: I. Computational Study with Detailed Chemistry", Kreutz, T. G., and Law, C. K., Paper No. 92 presented at the 1993 Joint Technical Meeting of the Central and Eastern States Sections of the Combustion Institute, New Orleans, LA March 15-17, 1993.
3. "Ignition in Nonpremixed Counterflowing Hydrogen versus Heated Air: II. Asymptotic Analysis with Reduced Mechanisms", Lee, S. R., and Law, C. K., Paper No. 93 presented at the 1993 Joint Technical Meeting of the Central and Eastern States Sections of the Combustion Institute, New Orleans, LA March 15-17, 1993.

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Report of Inventions

None

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3. Yetter, R. A., Dryer, F. A., and Rabitz, H., "A Comprehensive Reaction Mechanism for Carbon Monoxide/Hydrogen/Oxygen Kinetics", *Combustion Science and Technology*, Vol. 79, pp. 97 (1991).
4. Treviño, C. "Ignition Phenomena in H_2 - O_2 Mixtures", *Progress in Astronautics and Aeronautics*, pp. 19 (1990).

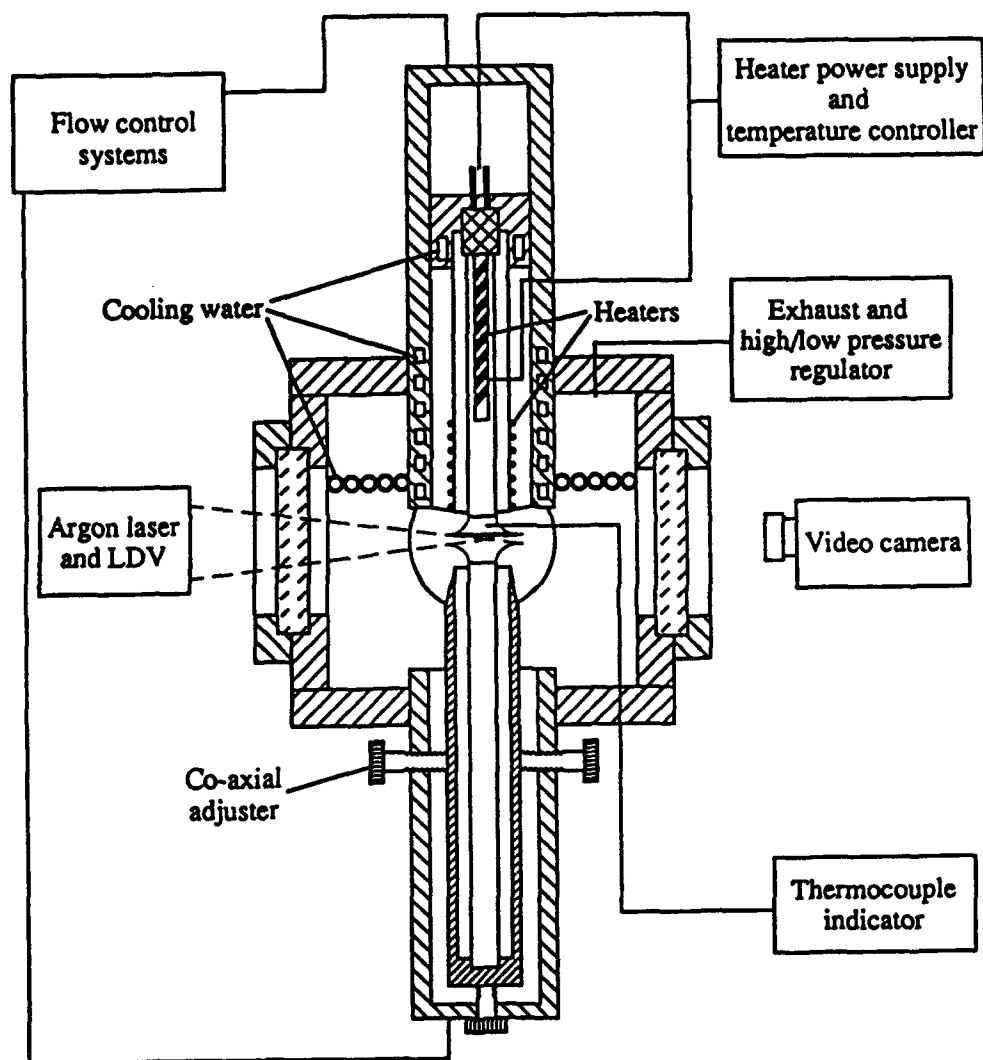


Figure 1: Experimental variable-pressure counterflow ignition apparatus.

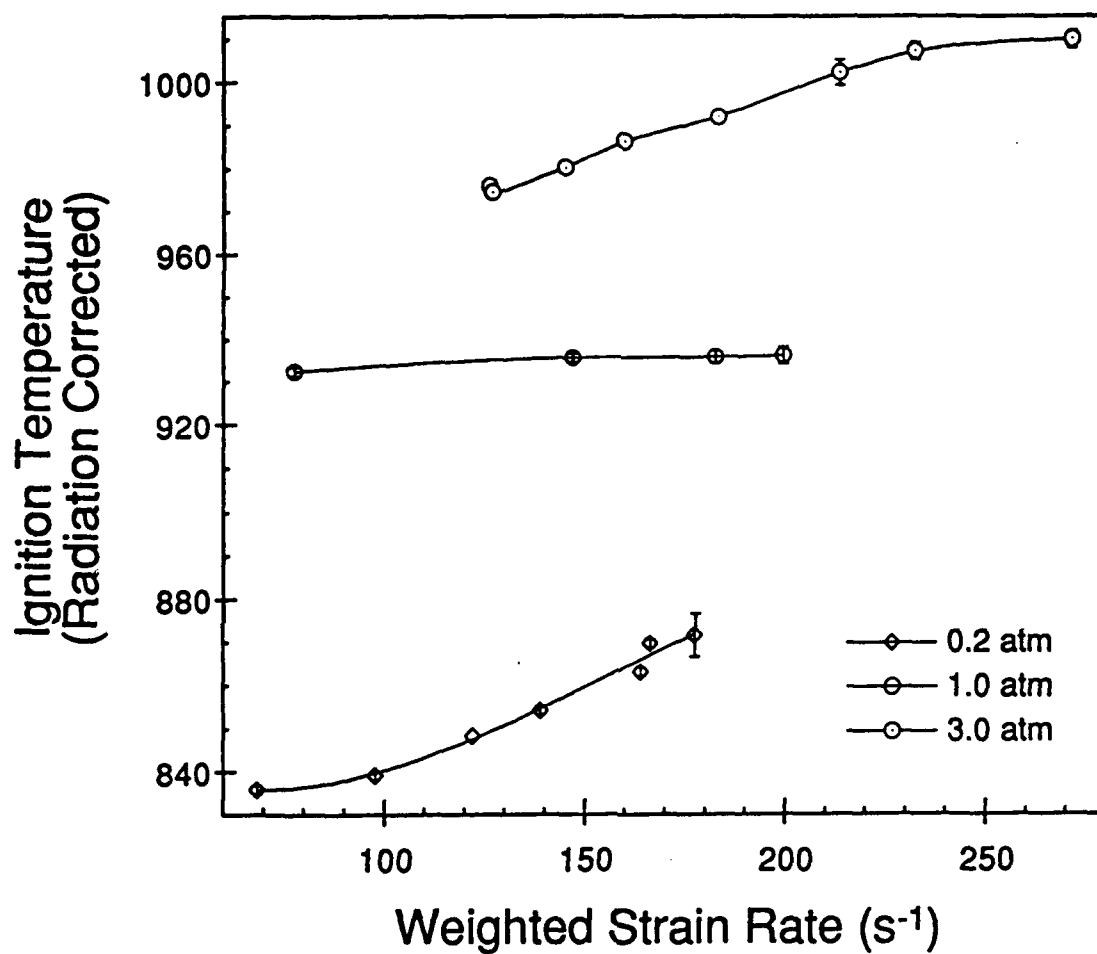


Figure 2: Experimentally measured temperatures as a function of pressure-weighted strain rate for three different pressures. Conditions: heated air flowing against a cold mixture of 20% H_2 in N_2 .

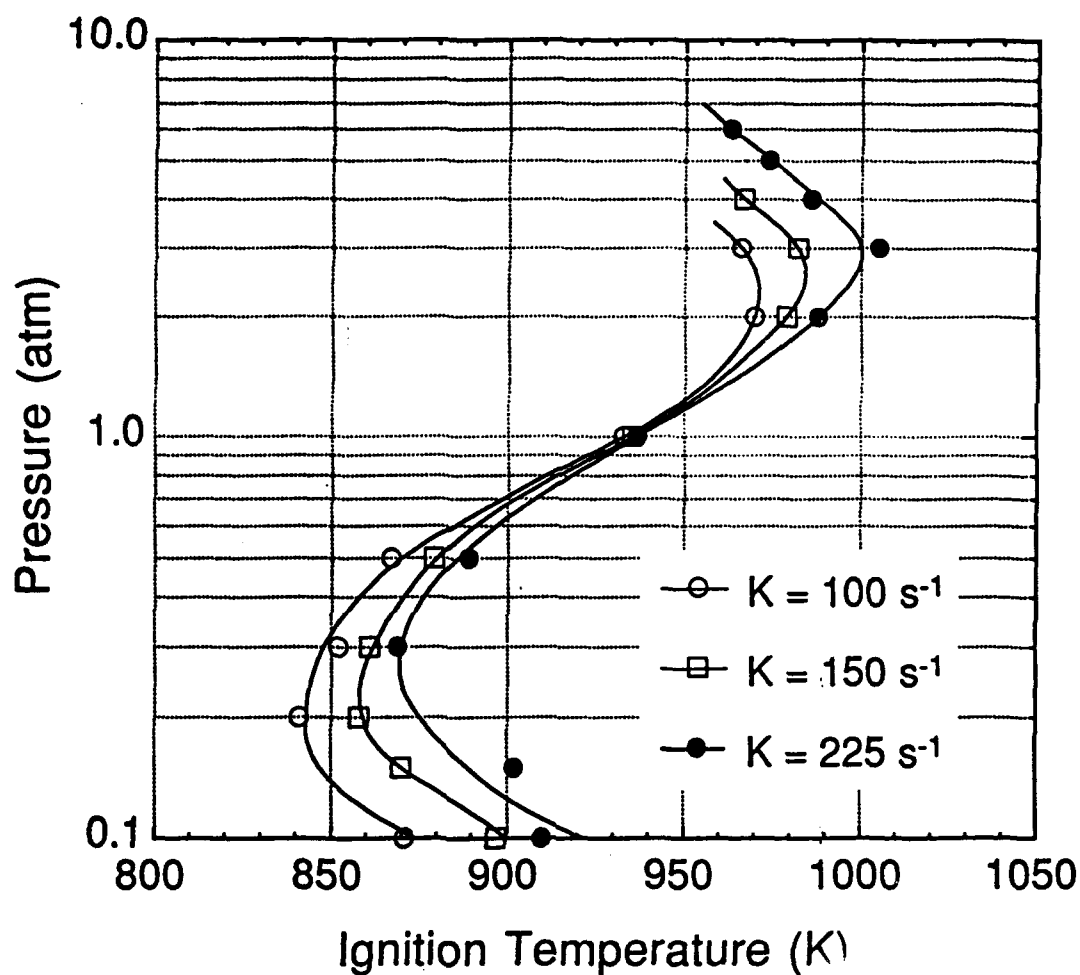


Figure 3. Experimentally measured ignition temperatures as a function of pressure for fixed values of pressure-weighted strain rate. Conditions: heated air flowing against a cold mixture of 20% H_2 in N_2 .

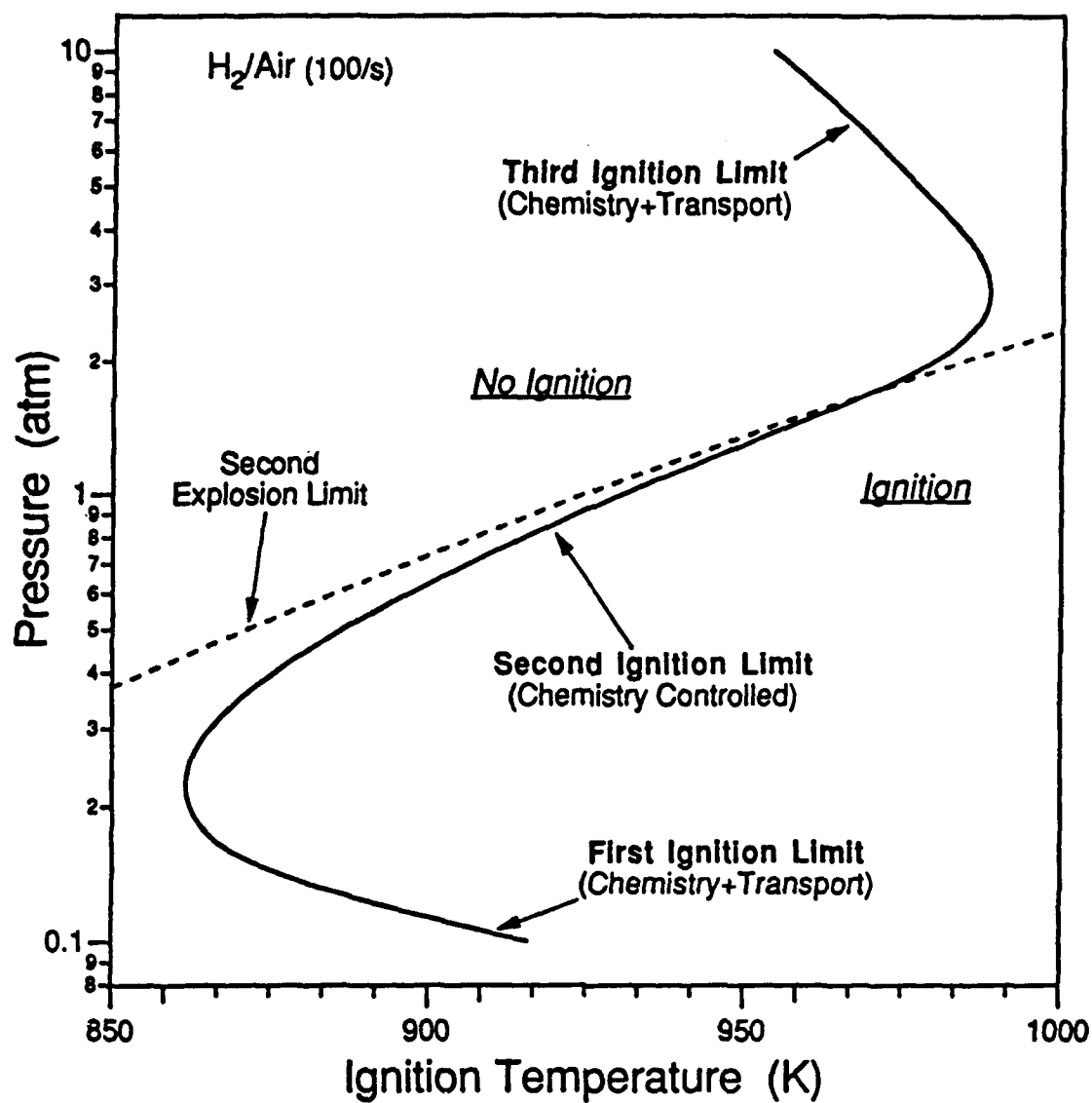


Figure 4. Calculated ignition temperatures as a function of pressure. Conditions: heated air flowing against a cold mixture of 60% H_2 in N_2 at a pressure-weighted strain rate of 100 s^{-1} .

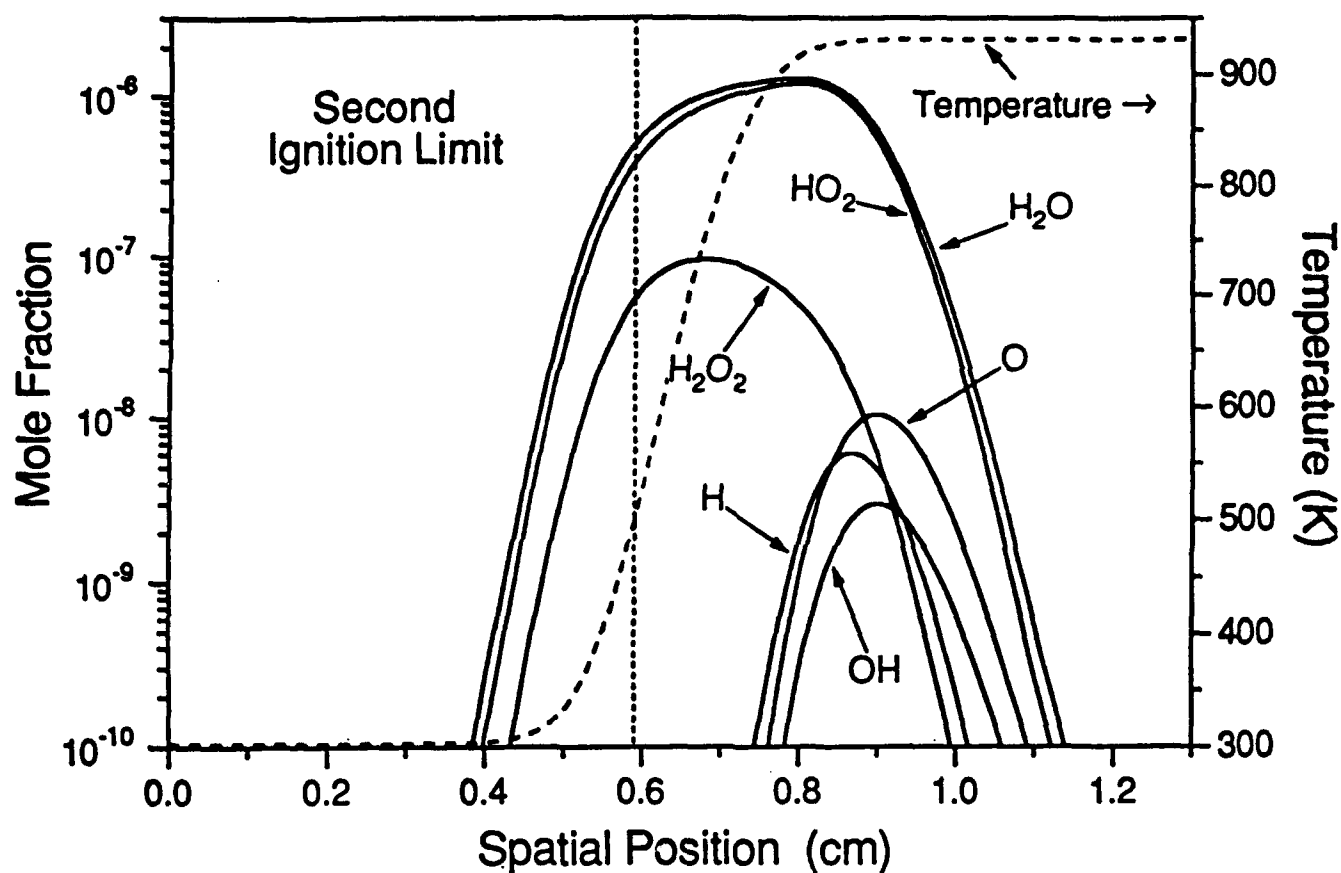


Figure 5. Spatially-resolved temperature and minor species concentration profiles in the second ignition limit ($p=1$ atm, $a=100$ s $^{-1}$, 60% H_2) just prior to ignition at $T_{\text{ign}}=930.7$ K. The dotted line corresponds to the stagnation plane of the counterflowing jets.

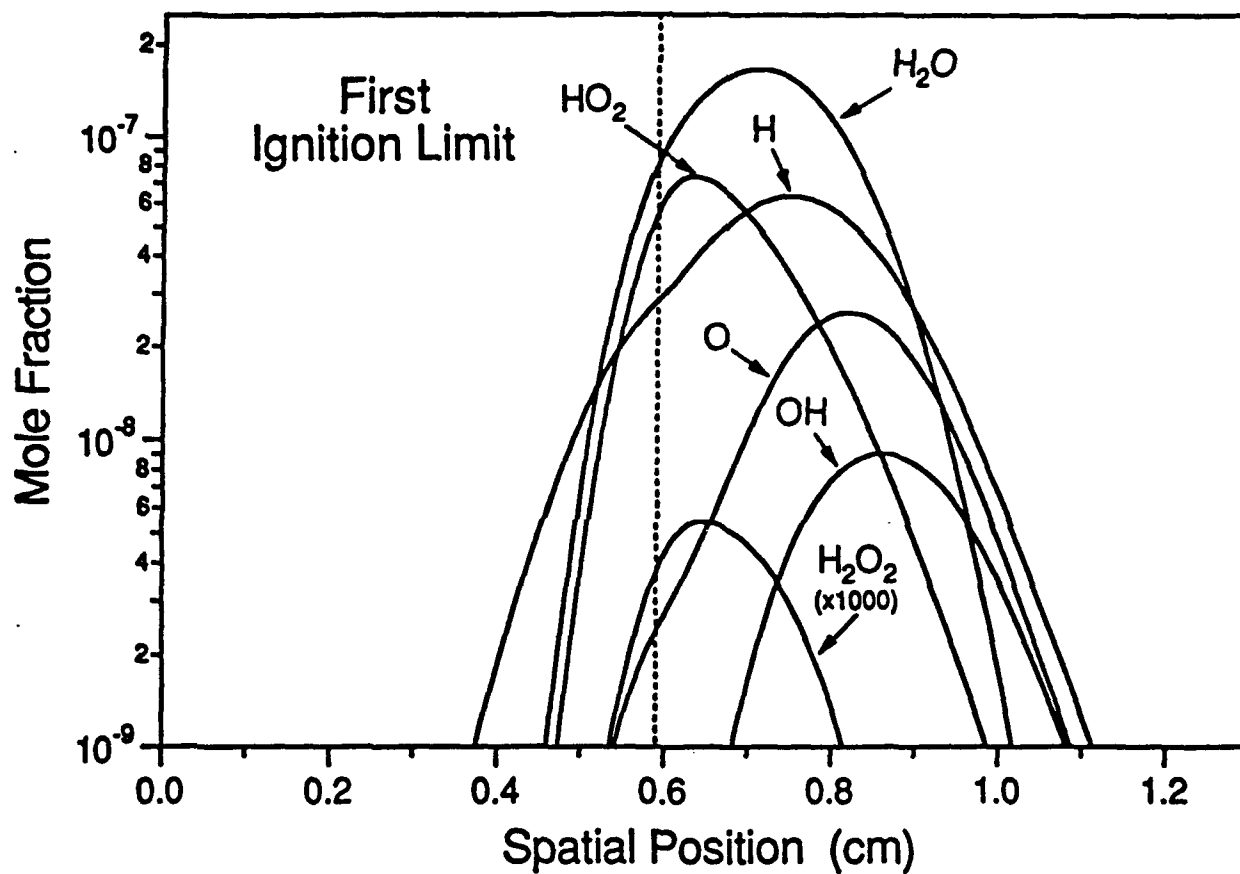


Figure 6. Spatially-resolved minor species concentration profiles in the first ignition limit ($p=0.1$ atm, $a=100$ s $^{-1}$, 60% H_2) just prior to ignition at $T_{\text{ign}}=915.8$ K.

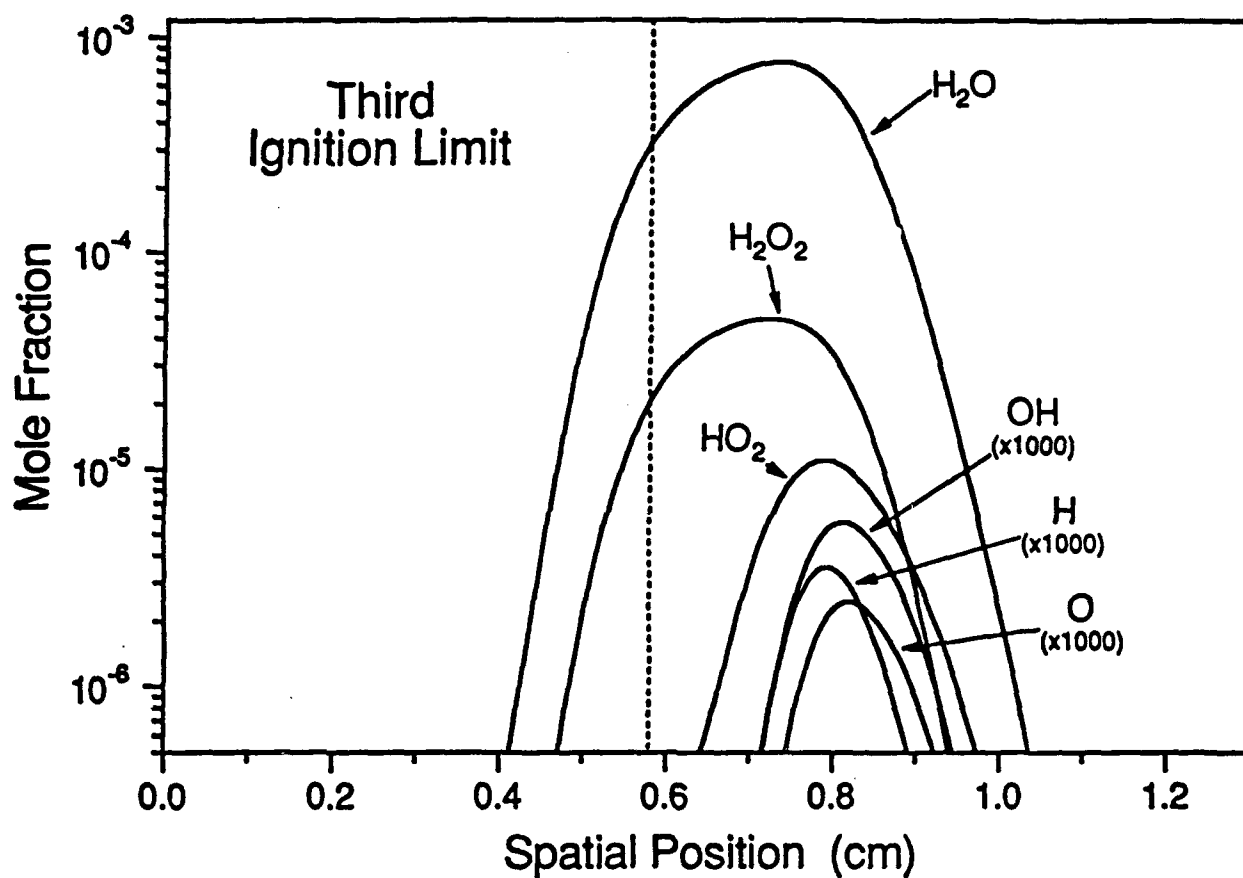


Figure 7. Spatially-resolved minor species concentration profiles in the third ignition limit ($p=10$ atm, $a=100$ s $^{-1}$, 60% H_2) just prior to ignition at $T_{\text{ign}}=954.3$ K.

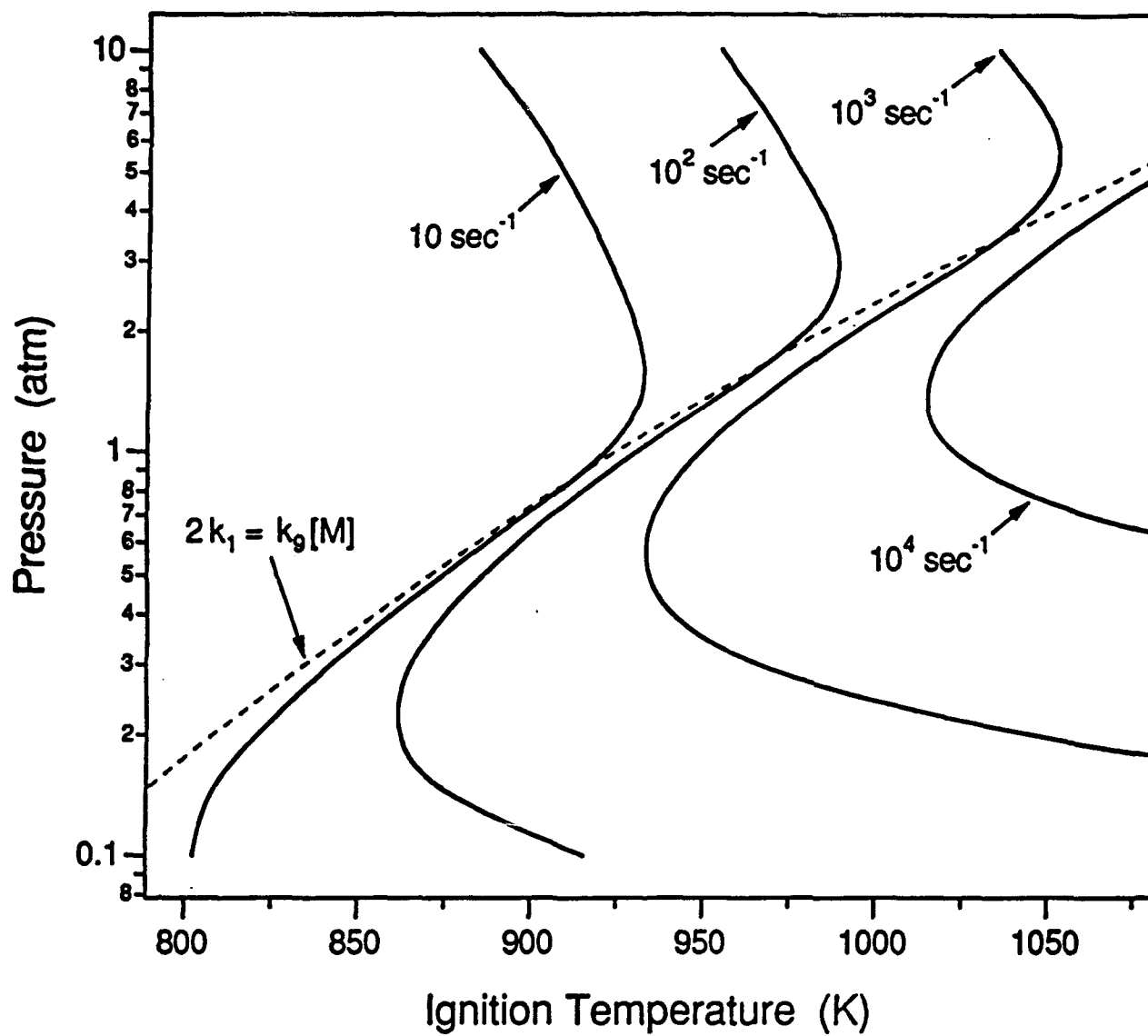


Figure 8. Ignition temperatures as a function of pressure and strain rate. Conditions: heated air flowing against a cold mixture of 60% H₂ in N₂.

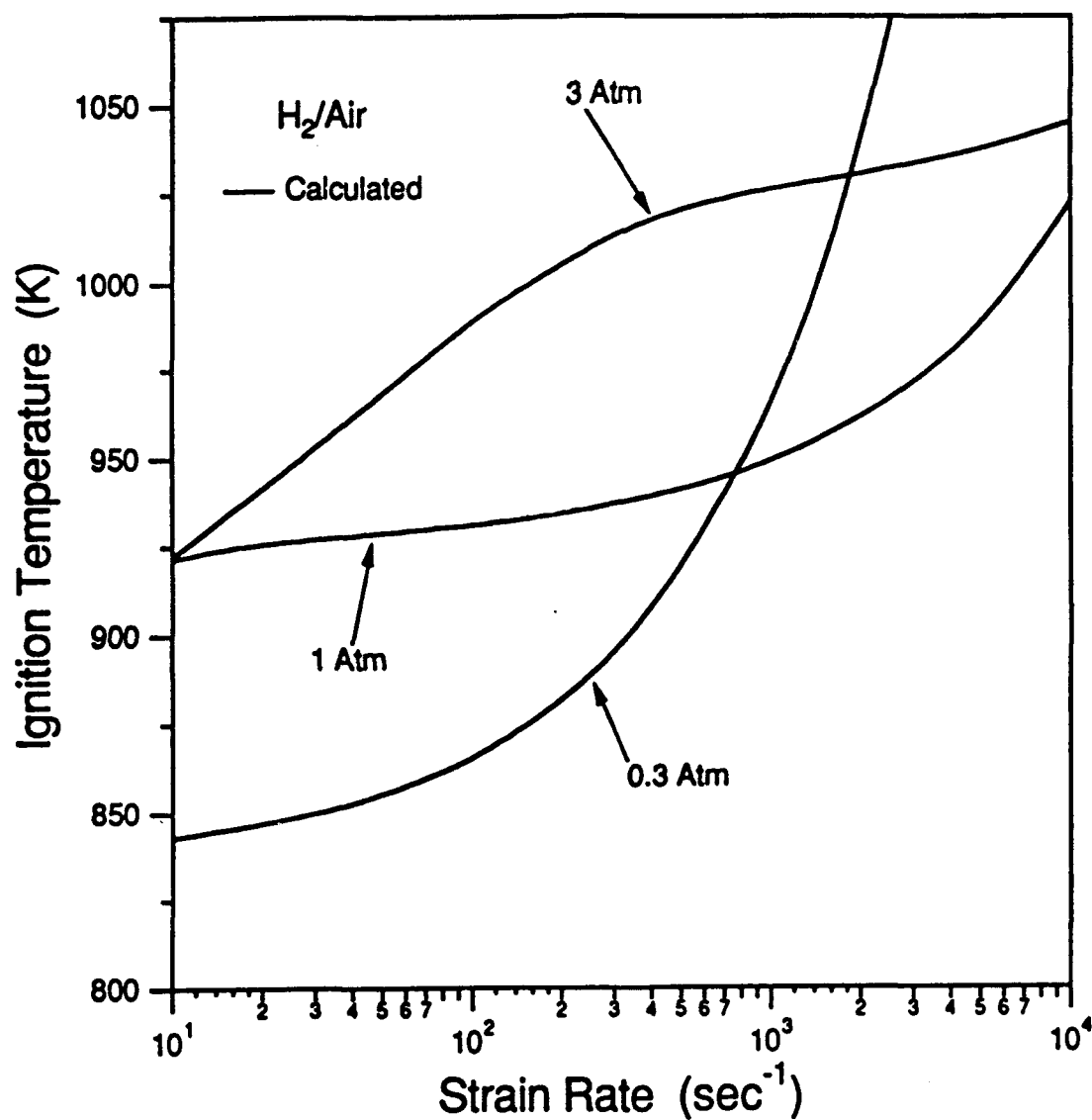


Figure 9. Ignition temperatures as a function of strain rate for three different pressures. Conditions: heated air flowing against a cold mixture of 60% H₂ in N₂.

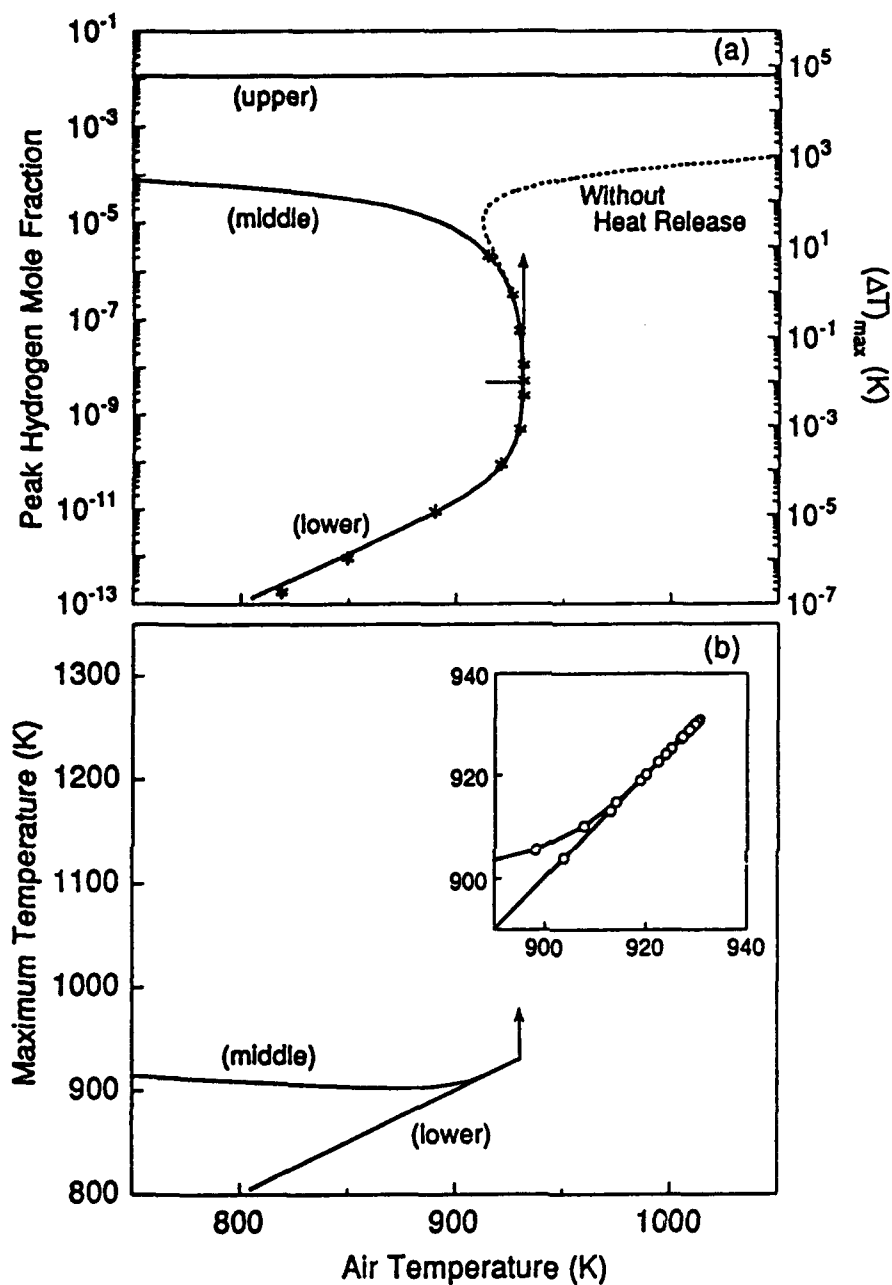


Figure 10. The peak hydrogen mole fraction, the maximum temperature of the system, and the local increase in temperature due to heat release graphed as a function of the air temperature for heated air flowing against a cold mixture of 60% H_2 in N_2 at a strain rate of 100 s^{-1} .

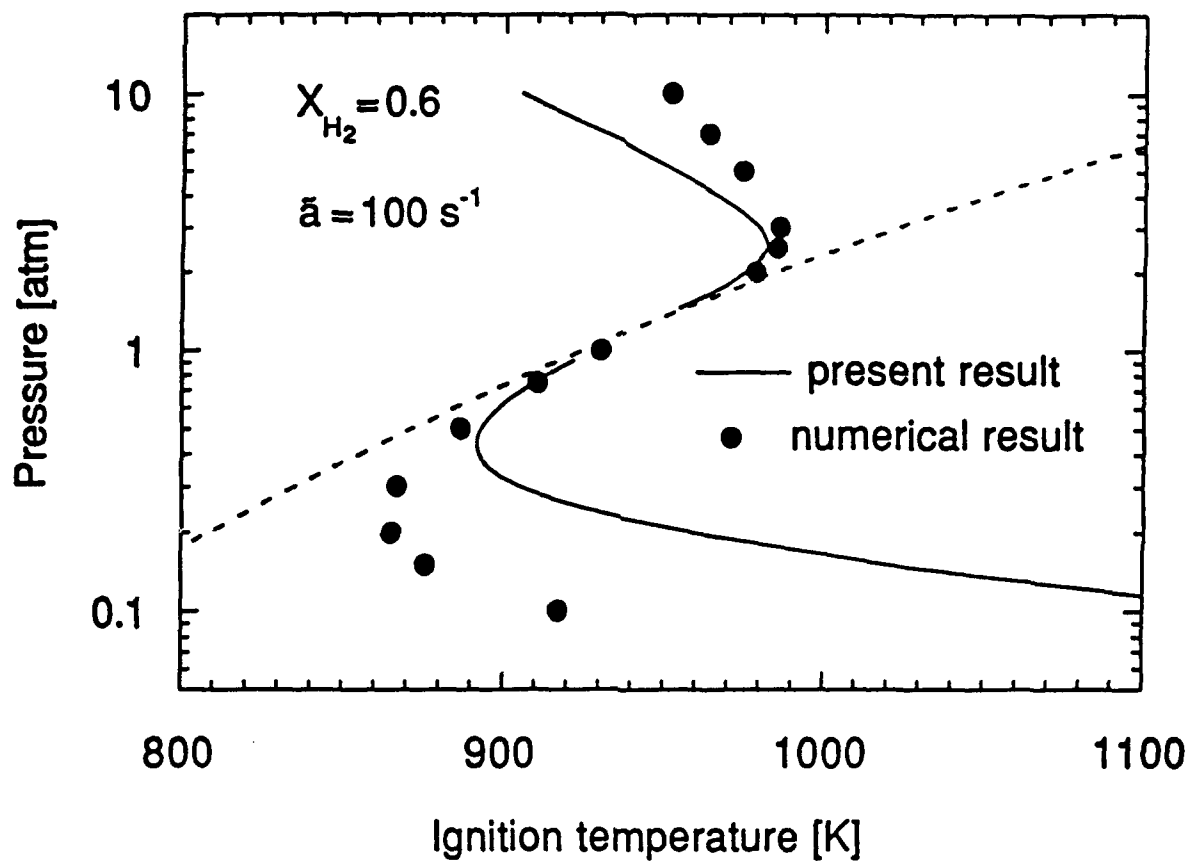


Figure 11. A comparison of ignition temperatures calculated using asymptotic analysis with reduced chemistry versus the numerical results using the full 19-step chemical reaction mechanism. Conditions: heated air flowing against a cold mixture of 60% H_2 in N_2 at a strain rate of 100 s^{-1} .